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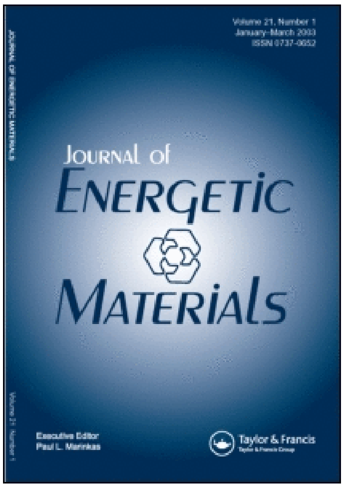

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CALCULATIONS OF HEATS OF FORMATION FOR NITROAROMATICS WITH PM3 AND MM2

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ABSTRACT

We have attempted to calculate heats of formation (ΔH_f°) for various aromatic nitro compounds with the semi-empirical molecular orbital theory and the molecular mechanics. As the results we may say that PM3, a semi-empirical MO method, and MM2, molecular mechanics, can estimate ΔH_f° of energetic materials with accuracy enough to use ΔH_f° for energy hazards prediction. In case of aromatic polynitro compounds, both methods may be able to calculate accurate ΔH_f°.

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INTRODUCTION

Energetic materials are widely used in various fields. In order to investigate characteristics of energetic materials, it should be indispensable to obtain their heats of formation(ΔH_f°). For example, heats of decomposition and heats of reaction can be calculated with ΔH_f°. We attempted to calculate ΔH_f° for several nitro compounds with the semi-empirical molecular orbital theory and the molecular mechanics, and showed their capability for ΔH_f° estimation[1]. As a result we realized that the effect of nitro groups should be estimated separately for aliphatic and aromatic compounds. Here, we conduct to calculate ΔH_f° for various nitro aromatic compounds with the semi-empirical molecular orbital theory and the molecular mechanics.

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METHOD

The programs used were MOPAC(Molecular Orbital Package) version 5.01[2] and MM2(Molecular Mechanics 2)[3]. Details of the method are described in our previous paper[1].

RESULTS and DISCUSSION

Structure

Calculated bond lengths and bond angles for p-nitrotoluene and m-nitroaniline are shown in Table 1. Good molecular geometries can be obtained with both methods. For most compounds in this work, the geometries calculated with MM2 correspond well with those with PM3.

TABLE 1-1

Geometry of p-Nitrotoluene Calculated with PM3 and MM2

Method	$C-CH_3$ (A)	C-N (A)	N-O (A)	∠ C-N-O (degree)	∠ O-N-O (degree)
obs.[4]	1.528	1.482	1.243	118.5	122.8
PM3	1.485	1.495	1.216	119.5	121.0
MM2	1.508	1.495	1.224	118.1	123.8

TABLE 1-2

Geometry of m-Nitroaniline Calculated with PM3 and MM2

Method	$C-NH_2$ (A)	$C-NO_2$ (A)	N-O (A)	∠ C-N-O (degree)	∠ O-N-O (degree)
obs.[4]	1.41	1.44	1.23	120	120
PM3	1.427	1.499	1.215	121.0	119.9
MM2	1.433	1.496	1.224	118.2	123.7

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Heat of Formation

Gas-phase heats of formation at 298K are calculated for aromatic nitro compounds with PM3 and MM2. Results are summarized in Table 2. Observed values are quoted from references[4-6].

Fig.1 shows ΔH_f° calculated with PM3 and MM2 in contrast to observed values. Both methods can estimate ΔH_f° very accurately. When ΔH_f° are expressed by cal/g, ΔH_f° are calculated within ± 50 cal/g from the observed value with PM3 ,and ± 40 cal/g with MM2. It shows that ΔH_f° calculated by PM3 and MM2 are accurate enough for using the estimation of heats of reaction for energetic materials. For example, gas-phase heats of decomposition calculated with ΔH_f° in Table 2 are -1380 cal/g(PM3), -1410(MM2) and -1420(observed) for 2,4,6-trinitrotoluene, and -1340 cal/g(PM3), -1400(MM2) and -1390(observed) for 2,4,6-trinitrophenol.

For 2,4-dinitrophenol and 2,4,6-trinitrophenol, ΔH_f° estimated with MM2 are much smaller than observed ones. By MM2, hydroxyl group is rather orthogonal to benzene ring, while by PM3 it is estimated to be planar. When MM2 geometry is used, ΔH_f° estimated with PM3 is -29.53 kcal/mol.

For several aliphatic polynitro compounds, ΔH_f° estimated with MM2 are rather different from the observed values because nitro groups are spatially very crowded and

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TABLE 2

Calculated Heats of Formation for Nitro Aromatics

Compound	ΔH_f°(kcal/mol)			
	PM3	MM2	obs.	AM1,corr.
Nitrobenzene	14.5	14.9	16.1	15.8
o-Dinitrobenzene	15.3	22.8	20.2	20.2
m-Dinitrobenzene	9.2	12.0	11.3	14.4
p-Dinitrobenzene	10.1	11.3	13.3	14.4
1,3,5-Trinitrobenzene	7.0	10.2	13.4	16.4
o-Nitrotoluene	9.6	8.7	9.3	9.5
m-Nitrotoluene	5.1	6.9	4.1	8.1
p-Nitrotoluene	4.7	6.9	7.4	7.8
2,4-Dinitrotoluene	2.1	4.2	4.7	7.5
2,6-Dinitrotoluene	9.2	10.8	9.6	11.3
2,4,6-Trinitrotoluene	4.0	9.5	12.3	16.2
o-Nitroaniline	12.8	16.5	15.2	15.2
m-Nitroaniline	12.5	17.3	16.5	18.5
p-Nitroaniline	10.7	17.3	16.2	16.1
2,4-Dinitroaniline	4.7	13.4	12.2	14.5
o-Nitrophenol	-33.2	-23.7	-29.3	-29.7
m-Nitrophenol	-29.9	-25.0	-28.0	-27.4
p-Nitrophenol	-31.7	-25.1	-25.4	-29.0
2,4-Dinitrophenol	-40.2	-26.7	-30.7	-32.3
2,4,6-Trinitrophenol	-39.3	-25.6	-25.9	-27.2
2,4-Dinitrochlorobenzene	6.6	13.0	17.8	14.0

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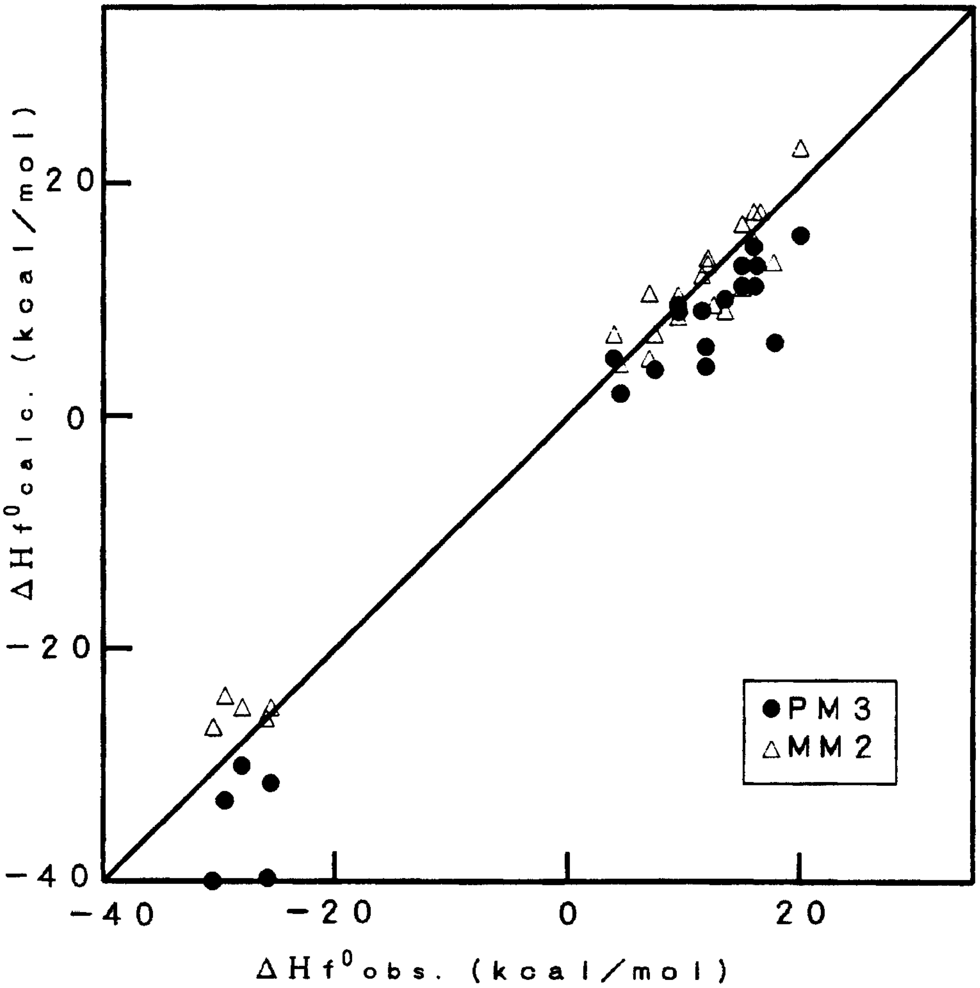

FIGURE 1

Calculated Heats of Formation for Nitro Aromatics with PM3 and MM2

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steric energy can't be appropriately evaluated in MM2[1]. To see the capability of PM3 and MM2 for aromatic polynitro compounds, ΔH_f° of polynitrobenzenes and polynitrotoluenes are calculated. The results are shown in Table 3.

Corrected AM1 values[4] (subtracting the constant value per one nitro group from ΔH_f° calculated with AM1 method) are also shown in the tables because there are few observed ΔH_f° for polynitro aromatics.

From Table 3, neighboring nitro groups in polynitrobenzenes raise ΔH_f° by about 10 kcal/mol. The values obtained with MM2 seem to be more accurate than those with PM3 from the comparison with corrected AM1 values. For polynitrotoluenes, both methods showed fairly good values. The interaction between methyl and nitro groups raises ΔH_f° by about 5 kcal/mol. In case of polynitro aromatics, which doesn't contain multi-nitro groups on one carbon atom, ΔH_f° can be predicted accurately in spite of the aromatic-ring constraint, though PM3 tends to give lower ΔH_f° and MM2, rather high ΔH_f°. Davis et al.[8] also calculated ΔH_f° for many kinds of nitro compounds with semi-empirical MO methods MINDO/3, MNDO and AM1. For polynitrobenzenes and toluenes, values with MINDO/3 are less than zero and those with MNDO are much larger than our data. PM3 is revised to reproduce the properties of nitro compounds[9] and PM3 seems to be the most reliable method to obtain ΔH_f° of all the

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TABLE 3

Calculated Heats of Formation for Polynitrobenzenes and Polynitrotoluenes

compound	ΔH_f°(kcal/mol) PM3	MM2	AM1,corr.
1,2,3-Trinitrobenzene	18.3	33.8	27.3
1,2,4-Trinitrobenzene	13.2	21.2	21.6
1,2,3,4-Tetranitrobenzene	24.1	45.3	34.1
1,2,3,5-Tetranitrobenzene	18.3	33.5	30.5
1,2,4,5-Tetranitrobenzene	19.6	32.2	39.3
Pentanitrobenzene	34.4	58.3	45.4
Hexanitrobenzene	45.9	78.1	60.4
2,3-Dinitrotoluene	8.1	17.2	13.0
2,5-Dinitrotoluene	4.9	4.9	8.1
3,4-Dinitrotoluene	5.4	14.7	11.6
3,5-Dinitrotoluene	-0.4	3.7	6.4
2,3,4-Trinitrotoluene	10.9	27.5	18.2
2,3,5-Trinitrotoluene	6.1	15.3	14.5
2,3,6-Trinitrotoluene	9.8	20.8	18.0
2,4,5-Trinitrotoluene	5.7	14.6	14.4
3,4,5-Trinitrotoluene	8.2	25.0	17.3
2,3,4,5-Tetranitrotoluene	16.7	40.3	27.0
2,3,4,6-Tetranitrotoluene	15.4	33.8	26.1
2,3,5,6-Tetranitrotoluene	15.6	32.4	27.0
Pentanitrotoluene	32.0	58.4	41.9

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semi-empirical MO methods.

Two-center bond energy can be calculated with PM3. It corresponds to the dissociation energy.[10] For polynitro aromatics, the more nitro groups substitute on the benzene ring, the less the absolute value of two-center bond energy and the bond order are, and the longer the bond length between carbon and nitrogen is. Similarly, in MM2 results, the more nitro groups there are, the longer the bond length between carbon and nitrogen is, and the larger the stretching energy of C-N bond is. These results suggest that polynitro aromatics become unstable or easy to decompose by the heat and the impact as the increase of the number of nitro groups.

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CONCLUSIONS

Heats of formation for aromatic nitro compounds have been calculated with the semi-empirical molecular orbital theory and the molecular mechanics. From our result we can say that PM3,semi-empirical MO method, and MM2,molecular mechanics, would estimate ΔH_f° within ± 50 cal/g of the observed value with PM3 ,and ± 40 cal/g with MM2. For polynitro aromatics, they would be good enough to estimate their energy hazards.

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